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(71) Applicant: **MEC CO., Ltd.**
Amagasaki-shi, Hyogo-ken (JP)

(72) Inventor: **Nakagawa, Toshiko,**
c/o MEC CO., LTD.
Amagasaki-shi, Hyogo-ken (JP)

(74) Representative: **Wächtershäuser, Günter, Prof. Dr.**
D-80331 München (DE)

(54) Etching solution for copper or copper alloy

(57) An etching solution for copper or copper alloys comprising, (a) sulfuric acid, (b) a persulfate, (c) at least one compound selected from imidazole, imidazole derivatives, pyridine derivatives, triazine, and triazine derivatives, and (d) water. The etching solution exhibits a high etching speed and does not oxidize the copper surfaces after etching.

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Description**BACKGROUND OF THE INVENTION**5 **Field of the Invention**

The present invention relates to an etching solution for copper or copper alloys which is useful for preventing rusting of the copper or copper alloy surfaces and for roughening these surfaces.

10 **Description of the Background Art**

In the manufacture of printed-wiring boards, copper surfaces are roughened in order to improve adhesion of resins such as etching resists or solder resists to be coated on the copper surfaces. Mechanical cleaning using a buffing or scrubbing machine or chemical cleaning, called microetching, are used for roughening copper surfaces. Chemical clean-
15 ing is more popular for treating substrates with fine line patterns.

Conventionally, persulfate-type etching solutions which comprise sulfuric acid and a persulfate have been used for chemical cleaning. These etching solutions have drawbacks such as a slow etching speed and a tendency for polished surfaces to be easily oxidized. Because of this, sulfuric acid-hydrogen peroxide type etching solutions which are free from these problems are being accepted in spite of the high cost.

20 However, the demand for persulfate-type etching solutions is not insignificant because of the low cost. There is a strong demand to solve of the above-mentioned problems associated with persulfate-type etching solutions.

SUMMARY OF THE INVENTION

25 The present inventors have conducted extensive studies in order to develop a low cost persulfate-type etching solution, and have found that an etching solution which exhibits a high etching speed and does not oxidize polished surfaces can be prepared by adding imidazole, an imidazole derivative, a pyridine derivative, triazine, or a triazine derivative.

Accordingly, an object of the present invention is to provide an etching solution for copper or copper alloys comprising,

- 30 (a) an inorganic acid,
(b) a persulfate,
(c) at least one compound selected from imidazole, imidazole derivatives, pyridine derivatives, triazine, and triazine derivatives, and
(d) water.

35 In a preferred embodiment of the present invention, said etching solution further comprises (e) amidosulfuric acid or an aliphatic sulfonic acid.

Other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

40 **DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS**

An inorganic acid is added to the persulfate-type etching solution for the purposes of stabilizing the etching speed and ensuring homogeneous etching without unevenness. Specific examples of the inorganic acid include sulfuric acid, hydrochloric acid, and the like. Sulfuric acid is preferred in view of the easiness in handling.

45 As examples of the persulfate used in the present invention as component (b), ammonium persulfate, potassium persulfate, sodium persulfate, barium persulfate, lithium persulfate, and the like can be given. The concentration of the persulfate can be selected from the range of 50 g/l to the saturated concentration of persulfate in the aqueous solution, and preferably from the range of 50-250 g/l. If this concentration is smaller than 50 g/l, sufficient etching capability cannot be exhibited, resulting in etched products with copper hydroxide remaining on the surface.

50 Component (c) for the etching solution of the present invention, which is a compound selected from imidazole, imidazole derivatives, pyridine derivatives, triazine, and triazine derivatives, is added to the etching solution for increasing the etching speed and preventing rust on the etched surfaces. Given as examples of the imidazole derivatives are 2-methylimidazole, 2-ethylimidazole, 2-propylimidazole, 2-aminoimidazole, 4-methylimidazole, 4-ethylimidazole, 4-propylimidazole, and the like. Examples of the pyridine derivatives include 2-methylpyridine, 2-aminopyridine, 2-aminomethylpyridine, 2-carboxypyridine, 4-methylpyridine, 4-aminopyridine, 4-aminomethylpyridine, and the like. 2,4-diamino-6-methyltriazine, 2,4-diamino-6-ethyltriazine, and the like are given as examples of the triazine derivatives. The concentration of component (c) in the etching solution is preferably 0.1-10 g/l, and more preferably 0.5-10 g/l, from the viewpoint of ensuring an acceptable etching speed and the solubility of the component (c) compounds.

Amidosulfuric acid or an aliphatic sulfonic acid may be further added to the etching solution of the present invention as component (e) to suppress decomposition of the persulfate. Methyl sulfonic acid, amino sulfonic acid, aminomethyl sulfonic acid, and the like can be given as examples of the aliphatic sulfonic acid. In view of the solubility of the component (e) in water, the concentration of component (e) in the etching solution is preferably 1-100 g/l, and more preferably 1-50 g/l.

5 Beside the above components, other various additives may be incorporated in the etching solution of the present invention. Such additives include, for example, fluorine-type or nonionic-type surfactants for reducing the surface tension of the solution, inorganic acid such as sulfuric acid and phosphoric acid for stabilizing the etching speed, and the like.

10 The etching solution of the present invention can be prepared by adding the above-mentioned components, at proportions described above, to water and blending the mixture. There are no specific limitations to the method of addition. The components may be added either all at one time or separately in any arbitrary order. Ion-exchanged water is preferably used as the water.

There are no specific limitations to the method of using the surface etching solution of the present invention. Examples include a method of spraying the solution to the surfaces of copper or copper alloy to be treated, a method of immersing the copper or copper alloy in the solution using an immersion conveyer, and the like.

15 The etching solution of the present invention can be widely used for chemical cleaning or the like of copper or copper alloys. For example, in the manufacture of multi-layered printed-wiring boards, it can be used for rust-removal and roughening prior to the oxide treatment of the copper surface, for roughening to improve the adhesiveness of etching resists and solder resists, and for rust-removal and roughening to improve the solderability. Recently, fluxes with a weak activity for which no post-washing with flon is necessary are widely used for soldering. Because the soldering using such fluxes is greatly affected by the surface conditions, the use of the etching solution of the present invention, which can perform 20 rust-removal, roughening, and rust-prevention at one time, is particularly effective as the pretreatment of such soldering. The etching solution of the present invention, of course, can be used for roughening and rust-prevention of a variety of materials made from copper or copper alloy.

25 Other features of the invention will become apparent in the course of the following description of the exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

EXAMPLES

Examples 1-8, Comparative Examples 1-5

30 Etching solutions were prepared by dissolving the components listed in Table 1 in water. Double-sided, copper-clad laminates for printed-wiring boards (FR-4) were immersed in a water bath containing the etching solution, stirred at 25°C, for 1 minute to examine the etching speed. After the etching, the laminates were left in an atmosphere at 40°C and 95% RH for 24 hours to macroscopically examine the formation of rust. The results are shown in Table 1, wherein 35 symbols in the column for rust formation have the following meanings.

AAA: No rust was formed.

BBB: Rust was slightly formed.

CCC: Rust was significant.

40 Examples 9-12, Comparative Example 6

Etching solutions were prepared by dissolving the components listed in Table 2 in water. To examine stability of the etching solutions, 10 g of copper was dissolved in the solutions and the etching speeds were measured in the same manner as in Example 1, immediately after copper was dissolved and after storing the solution for 24 hours. The results 45 are shown in Table 2.

The etching solution of the present invention is made from an inexpensive persulfate as a major component, and yet exhibits a high etching speed and an effect of preventing rust on the etched surface.

TABLE 1

| | Component (g/l) | Etching speed ($\mu\text{m}/\text{min}$) | Rust formation |
|-----------|--|--|----------------|
| Example 1 | Sodium persulfate 165.0 Sulfuric acid 30.0 Imidazole 2.0 Ion-exchanged water Balance | 1.5 | AAA-BBB |
| Example 2 | Sodium persulfate 165.0 Sulfuric acid 30.0 2-Methylimidazole 2.0 Ion-exchanged water Balance | 2.3 | AAA |
| Example 3 | Sodium persulfate 165.0 Sulfuric acid 30.0 4-Methylimidazole 2.0 Ion-exchanged water Balance | 2.4 | AAA |
| Example 4 | Sodium persulfate 165.0 Sulfuric acid 30.0 2-Aminopyridine 2.0 Ion-exchanged water Balance | 2.0 | AAA |
| Example 5 | Sodium persulfate 165.0 Sulfuric acid 30.0 4-Aminopyridine 2.0 Ion-exchanged water Balance | 2.0 | AAA |
| Example 6 | Sodium persulfate 165.0 Sulfuric acid 30.0 2,4-Diamino-6-methyltriazine 2.0 Ion-exchanged water Balance | 4.0 | AAA-BBB |
| Example 7 | Ammonium persulfate 200.0 Sulfuric acid 30.0 4-Methylimidazole 2.0 Ion-exchanged water Balance | 0.9 | AAA |
| Example 8 | Ammonium persulfate 165.0 Sulfuric acid 30.0 2-Methylimidazole 2.0 Amidosulfuric acid 10.0 Ion-exchanged water Balance | 1.1 | AAA |

TABLE 1 (Continued)

| | Component (g/l) | Etching speed ($\mu\text{m}/\text{min}$) | Rust formation |
|-----------------------|---|--|----------------|
| Comparative Example 1 | Sodium persulfate 165.0 Sulfuric acid 30.0 Ion-exchanged water Balance | 0.7 | CCC |
| Comparative Example 2 | Sodium persulfate 165.0 Sulfuric acid 30.0 Benzotriazole 2.0 Ion-exchanged water Balance | 0.2 | AAA |
| Comparative Example 3 | Sodium persulfate 165.0 Sulfuric acid 30.0 1,2-4-Tetrazole 2.0 Ion-exchanged water Balance | 2.2 | CCC |
| Comparative Example 4 | Sodium persulfate 165.0 Sulfuric acid 30.0 Pyridine 2.0 Ion-exchanged water Balance | 0.3 | AAA |
| Comparative Example 4 | Sodium persulfate 200.0 Sulfuric acid 30.0 Ion-exchanged water Balance | 0.3 | CCC |

TABLE 2

| | Component (g/l) | | Etching speed ($\mu\text{m}/\text{min}$) | | Decrease (%) |
|-----------------------|---------------------|---------|--|----------------|--------------|
| | | | After preparation | After 24 hours | |
| Example 9 | Sodium persulfate | 165.0 | 2.5 | 2.2 | 12 |
| | Sulfuric acid | 30.0 | | | |
| | 4-Methylimidazole | 2.0 | | | |
| | Methylsulfonic acid | 10.0 | | | |
| | Ion-exchanged water | Balance | | | |
| Example 10 | Sodium persulfate | 165.0 | 2.6 | 2.4 | 8 |
| | Sulfuric acid | 30.0 | | | |
| | 4-Methylimidazole | 2.0 | | | |
| | Amidosulfuric acid | 10.0 | | | |
| | Ion-exchanged water | Balance | | | |
| Example 11 | Sodium persulfate | 165.0 | 2.5 | 2.1 | 16 |
| | Sulfuric acid | 30.0 | | | |
| | 4-Methylimidazole | 2.0 | | | |
| | Taurine * | 10.0 | | | |
| | Ion-exchanged water | Balance | | | |
| Example 12 | Sodium persulfate | 165.0 | 1.0 | 1.0 | 0 |
| | Sulfuric acid | 30.0 | | | |
| | 4-Methylimidazole | 2.0 | | | |
| | Amidosulfuric acid | 10.0 | | | |
| | Ion-exchanged water | Balance | | | |
| Comparative Example 6 | Sodium persulfate | 165.0 | 2.2 | 1.4 | 36 |
| | Sulfuric acid | 30.0 | | | |
| | 1,2,4-Tetrazole | 2.0 | | | |
| | Ion-exchanged water | Balance | | | |

* Aminoethanesulfonic acid

Claims

1. An etching solution for copper or copper alloys comprising,

- (a) sulfuric acid,
- (b) a persulfate,
- (c) at least one compound selected from imidazole, imidazole derivatives, pyridine derivatives, triazine, and triazine derivatives, and
- (d) water.

2. The etching solution according to claim 1, further comprising (e) amidosulfuric acid or an aliphatic sulfonic acid.



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EUROPEAN SEARCH REPORT

Application Number
EP 95 11 2324

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
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| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
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| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| | | | C23F C23G |
| The present search report has been drawn up for all claims | | | |
| Place of search | | Date of completion of the search | Examiner |
| THE HAGUE | | 6 November 1995 | Torfs, F |
| CATEGORY OF CITED DOCUMENTS | | | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | |

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